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A Study Of The Electrodeposition Of Lead.

**A STUDY OF THE ELECTRODEPOSITION
OF LEAD**

BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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Up to the present there has been no good explanation offered for the effect of "addition reagents" in the formation of smooth deposits of metals from electrolytes which normally yield rough, non-adherent ones. The practice in electroplating and electrorefining has been almost entirely empirical. The present industries of electroplating are the result of a vast number of experiments made with no guiding theory.

Particularly interesting, in this connection, is the effect of " addition reagents " in the deposition of lead, which is the subject of this investigation. In a cell with lead electrodes and an electrolyte of either lead perchlorate or fluosilicate, lead deposits in a coarse, crystalline, non-adherent form, which later develops into spongy, treelike masses, which fall from the cathode to the bottom of the cell. In the Bett's process, glue, to the extent of a few hundredths of one percent, is added to the lead fluosilicate electrolyte and a smooth, firm deposit results. An explanation of this rather surprising effect of the addition of a small amount of a foreign substance to the electrolyte would, obviously, be interesting and important, especially if the explanation could also be extended to apply to the formation of smooth deposits of other metals.

There have been some experiments carried out with the view of explaining the effect of foreign substances on the electrodeposition of silver, by Rosa, Vinal, and McDaniel. *

* Bureau of Standards, 9, 209, (1912).


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They undertook this investigation in connection with their study of the silver voltometer. In their study of the effect of addition reagents on the electrodeposition of silver, they found that dextrose, invert sugar, formaldehyde, and various other reducing agents, when present, gave a larger number of crystals or uncrystalline masses, the stronger reducing agents giving the greater effect.

They also prepared colloidal silver by adding concentrated water extracts of filter paper to the silver nitrate solutions. These colloidal solutions lasted as long as two months and, were very similar to colloidal solutions prepared by other methods. It was thought that the permanancy of these solutions was due to the " protective colloid " effect of the filter paper extract present. They concluded that the colloidal silver was the agent that modified the character of the deposits. They further prepared Bredig's colloidal silver, which when added to a silver nitrate solution,, gave more crystals in the cathode deposit. The colloidal metal was also shown to migrate to the cathode.

Mathers and Kuebler * made an investigation of the action of addition reagents in restraining the characteristic loosely-adherent, crystalline structure of the electrodeposited silver from silver nitrate solution, with the end in view of discovering, if possible, a method of forming solid, smooth, and adherent silver cathodes. These investigators found that several organic substances such as aqueous extract of filter paper, pine wood shavings, silk, cotton etc., caused the deposits to be more

* Transactions of Amer. Electrochem. Soc. Advance Copy. Apr. 29, 1916.



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or less non-crystalline or imperfectly crystalline. The same effect was produced by glue, Bredig's colloidal silver, and by additions of hydrazine, dextrose, formaldehyde, phenol, etc. According to Mathers and Kuebler all of these substances which affect the silver deposit have the power of reducing solutions of silver nitrate to colloidal silver. All of the organic acids tried in this work had an influence on the deposits, which in most cases were made more finely crystalline and coherent. Only tartaric acid and citric acid gave smooth deposits showing little or no crystalline structure. One important effect is the beneficial effect on the nature of the deposit, of large amounts of tartaric acid. As smooth deposits can be formed in the presence of free nitric acid, Mathers and Kuebler do not favor the theory advanced by Rosa, Vinal, and McDaniel.

There have been many other investigations on the effects of " addition reagents ", but the investigators do not discuss explanations of these effects.

Traube-Mengarini and Scala** came to the conclusion, as a result of their experiments, that lead, copper, and iron form colloidal solutions by merely allowing the metals to stand in contact with water. These metallic colloids are, however, oxidized if the air were not excluded. Our first working hypothesis was that the colloidal particles form, as described, from the metal electrodes, deposit on the cathode and become nuclei for crystal-formation. A large number of small crystals, thus formed,

would obviously result in a firmer, finer grained deposit.

The addition reagent, glue, may thus have one or both of two effects. First it may have the same effect as reducing substances, which, according to this hypothesis, is to absorb the oxygen present, thus preventing the oxidation of the metallic colloid. In this way crystal-nuclei would be kept in the metallic state and smooth deposits formed. Secondly, the glue may act as a " protective colloid " on the colloidal lead particles. In this protective effect, the glue, which forms a colloidal solution, is thought to surround the colloidal particles and completely protect them from oxidation. On the basis of this hypothesis, if no oxygen were present, addition reagents would be entirely unnecessary.

Accordingly a series of experiments was undertaken to compare the deposits produced by the electrolysis of solutions, from which the air has been pumped, and solutions containing air. It was necessary, in the air free solution, to keep the anode and cathode portions from mixing, since oxygen or an oxidizing substance might form at the anode. This, according to the hypothesis, would oxidize the colloidal neuclei and spoil the deposit.

An "H" shaped tube was first tried, in which an electrode was placed in each upright tube. The upright tubes were stoppered and suction pump connections made to each tube from which the air was removed. A similar "H" tube was placed in series with this, but was not connected to a pump. On the electrolysis of the two solutions almost identical deposits were obtained from both solutions, although the deposit from the air-

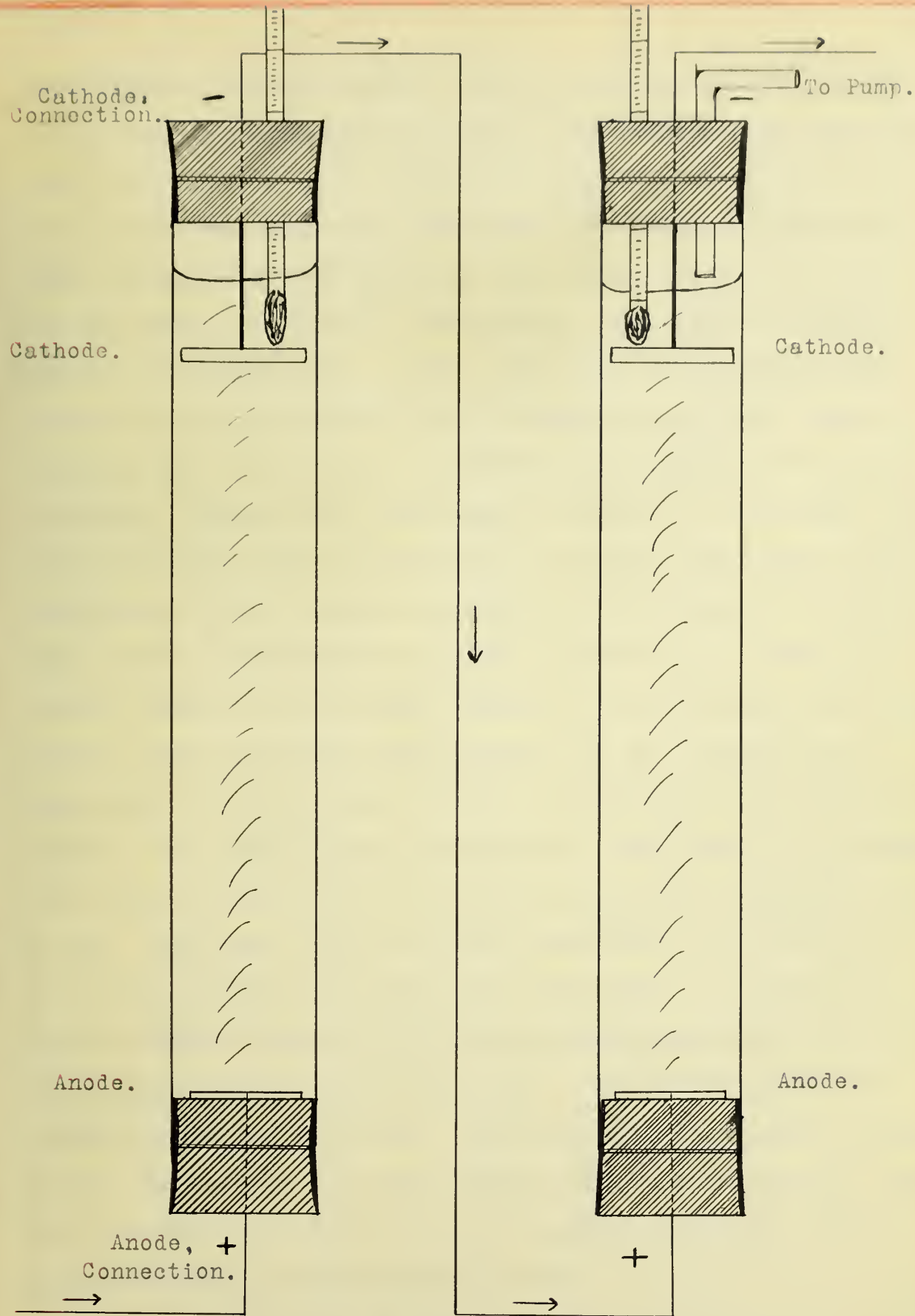


Figure 1.

free solution seemed somewhat smoother and less crystalline at times. In this arrangement, however, the results were uncertain since the solution under suction was stirred by boiling in the horizontal connecting tube, thus mixing the electrode portions. Next the separation of the anode and cathode by means of a porous cup was tried, the one cell being placed in a vacuum desiccator and the air pumped out. In this case vapor was formed in the pores of the cup and raised the resistance so that the current fluctuated and the potential drop in the two cells in series was different. Finally the cells shown in Figure 1. were used. In designing these cells, consisting of vertical glass tubes, with the cathode at the top and the anode at the bottom, we had the same object in view as above, which was to keep the anode and cathode portions from mixing. During the electrolysis the cathode portion would naturally become lighter as the lead ions were taken from it and the anode portion would become more dense because of the lead entering the solution. Thus having the cathode above and the anode below there would naturally be less tendency to mix. The anode portion was also immersed in an ice bath so as to keep it cool and consequently more dense. As before the air was removed from one cell and the other was open to the air. A May-Nelson pump was used which was capable of lowering the pressure to two millimeters. There was never any marked difference in the deposit from the solution under suction and the one from the solution containing air. Sometimes one formed more treelike masses and sometimes the other.

Along with the above experiments attempts were made to repeat Traube-Mengarini and Scala's work of preparing metallic

colloids by allowing metals to stand in water. On putting lead foil in a tube of redistilled water a slight turbidity resulted. But if the water was first boiled under reduced pressure and the lead then dropped in (still under reduced pressure) a slight turbidity appeared only very slowly, probably due to the slow leaking in of air. This turbidity is, no doubt, due to the formation of lead oxide or hydrate. On repeating this experiment, but by evacuating the solution before dropping in the lead, it could be seen that the lead caused only turbidity. As a comparison a similarly treated tube of redistilled water was prepared. Under the Ultra-microscope the distilled water showed only an occasional colloidal particle. The water boiled in contact with lead, under partial vacuum, (20 milli-meters), showed a larger number of the colloidal particles, but not more than could be accounted for by a possible trace of oxygen remaining in the solution. In order to be certain whether colloidal metallic lead forms in the absence of oxygen, we must, then, bring the lead in contact with water from which every trace of air is excluded. To do this three glass tubes about two centimeters in diameter and ten inches long were procured. In one tube was placed a small thin walled sealed tube containing lead foil and air. The large tube was left open, filled with water, and the small tube containing the lead, broken. In the second large tube was placed a small, thin walled, evacuated tube containing lead. The large tube was filled with redistilled water and sealed while the water was boiling and the steam escaping. By vigorous shaking the small inner tube was broken, thus exposing the lead to the water. For comparison a large tube was filled with redistilled water and

Fig.2

put through the same processes as the other. In about ten days the tubes were examined. The tube containing only water was unchanged. The "lead in the presence of air" tube showed a small amount of white colloidal appearing material which had settled to the bottom, but which, when shaken, remained in suspension for some time. In the "lead in the absence of air" tube the lead was apparently unaffected and no colloidal material was visible.

About this time Nordenson's*work was called to our attention. His conclusions may be summarized as follows:- "A direct spontaneous solution of metals as metallic colloids never occurs. Neither will such solutions be formed by long standing, by boiling, nor by heating the metal to a high temperature followed by a sudden plunging in the liquid. In the case of metals which can easily be oxidized, oxides or hydrates will be formed by the action of small amounts of oxygen, and these on account of their low solubility appear as colloids. Especially in the case of lead is this oxidation extremely vigorous, but the metallic colloid is not formed. Silver is dissolved in water through oxidation to the oxide. Here, as with lead, the colloid is formed secondarily as a result of a chemical change. The unoxidizable metals gold and platinum remain wholly unchanged. The other metals copper, zinc, iron, nickel, cobalt, chromium, manganese, bismuth, tin, aluminium, magnesium and cadmium are attacked more or less, according to their affinity for oxygen, and the resulting compounds appear at times like colloids, but are not reduced. Their metallic colloids are not formed." Nordenson's work confirms the conclusions from our experiments. Traube-Mengarini and Scala were evidently in error in thinking that oxygen was excluded from the water they used.

* Kolloidchemische Beihefte, Band 7, Heft 4-5, (1915).

It may thus be concluded that, since the removal of oxygen does not affect the deposits and since colloidal metal particles do not arise from the contact of the metals with water, the crystal-nuclei, which are probably responsible for the formation of smooth deposits, cannot come from the electrodes.

It now seemed more probable that the effects of reducing " addition reagents " was to produce metallic colloids from the salts in the electrolyte. Certain addition reagents also appear to have the property of protecting such colloids once they have been formed. For instance, smooth deposits of silver can be produced from silver salts to which the reducing substances potassium cyanide or tartaric acid have been added. The latter substance will, as is well known, produce colloidal silver from ammoniacal silver nitrate solution. This mixture of silver nitrate, ammonia, and tartaric acid will, it will be recalled, form smooth deposits of silver on glass or metal surfaces without the aid of electrolysis. In cases where glue or gelatine are the effective agents for producing smooth deposits, it seems probable that the effect is a combination of the reduction, and the protection of the resulting colloids, by these substances.

In order to test out this theory, in the deposition of lead, a number of small beakers were used as cells and lead electrodes inserted in each. In one experiment six cells, with lead electrodes and lead fluosilicate as the electrolyte, were put in series and the following addition reagents added. To cells (1) and (2) was added alcohol, in different amounts; in (3) a few drops of ether; in (4) some silicic acid; in (5) silicic acid and alcohol and in (6) silicic acid and ether. After twenty minutes the

deposits in cells (2), (3) and (6) appeared to be smoother. At the end of one hour and ten minutes cell (6) had the smoothest deposit of all. Another series of cells was electrolysed, using the same reagents as in cells (4), (5), and (6), but in larger quantities, with practically the same results.

From these qualitative experiments it appears that lead deposits are improved, (a) by the addition of reducing agents, and (b) by the addition of silicic acid, which may in the present case act as a protective colloid. That the improvement is due to the reducing nature of some reducing agents is shown by the following experiments.

The cathode deposits were observed in three cells in series, all containing the lead fluosilicate electrolyte. Cell number (1) contained no addition reagent; cell (2) glucose, a non-reducing sugar; and cell (3) dextrose, a reducing sugar. The deposits in cells (1) and (2) were almost identical and showed a great deal of the "treeing" effect. Cell number (3) gave a fairly smooth deposit. This in connection with the results above, would indicate that the improvement of deposits is at least partially due to the reducing effect of the addition reagent. This experiment was repeated several times always with the same results. The current density was always about 0.36 amperes per square decimeter and the experiments were made at room temperature.

Another experiment was made to further test the effect of silicic acid when added to solutions containing a reducing addition reagent. Six cells in series were used. Number (1) was a cell of the lead fluosilicate electrolyte without any addition reagent. Number (2) contained 0.1 gram of dextrose as addition

reagent to fifty cubic centimeters of the electrolyte. Number (3) contained 0.2 grams of dextrose to the same amount of electrolyte. To number (4) was added 0.1 gram dextrose and one cubic centimeter of silicic acid solution. Number (5) contained 0.1 gram of dextrose and two drops of silicic acid solution, and number (6), 0.1 gram of dextrose and ten drops of the silicic acid solution. The current density was about 0.36 amperes per square decimeter. The usual "treeing" was observed in the first cell; a little better deposit with 0.1 gram of dextrose addition reagent; a still better deposit with the 0.2 grams of dextrose addition reagent. The cell with 0.1 gram of dextrose and two drops of silicic acid solution was considerably better than the first three, and the next with 0.1 gram of dextrose and ten drops of silicic acid solution was better yet. The cell containing 0.1 gram dextrose and one cubic centimeter of silicic acid solution gave the best deposit of all and it was a fairly smooth and very adherent deposit.

It appears, then, that the silicic acid solution addition reagent probably has the effect of a protective colloid. On account of the importance of this result the experiment was carried out several times with identical results each time. However, further work will be done on this subject. The effect of the addition of glue is probably the same as that of the addition of both silicic acid and dextrose, that is, it has the effect of reducing to metallic colloid and protecting the resulting colloid.

In conclusion, our experiments up to the present can best be explained by the theory as outlined on page (8).

S U M M A R Y

1. Nordenson's conclusion, that colloidal metals do not form when metals are allowed to stand in contact with water, has been confirmed in the case of lead.

2. Smooth deposits do not form as the result of crystal nuclei originating directly from the metal of the electrodes, as has been shown by the electrolysis of air-free solutions.

3. The most plausible theory for the explanation of the improvement of metal deposits is that the addition reagents produce colloidal metal by reduction of the metal salts in the electrolyte, and that this, in certain cases, is followed by a protective action on the part of the addition reagent if it is a colloid. The glue used in the electrorefining of lead probably acts both as a reducing agent and as a protective colloid.

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